

Fluctuation theorems for non-Markovian quantum processes

B. Leggio,^{1,2} A. Napoli,¹ H.-P. Breuer,² and A. Messina¹

¹*Dipartimento di Fisica e Chimica, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy*

²*Physikalisches Institut, Universität Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg, Germany*

(Dated: January 9, 2013)

Exploiting previous results on Markovian dynamics and fluctuation theorems, we study the consequences of memory effects on single realizations of nonequilibrium processes within an open system approach. The entropy production along single trajectories for forward and backward processes is obtained with the help of a recently proposed classical-like non-Markovian stochastic unravelling, which is demonstrated to lead to a correction of the standard entropic fluctuation theorem. This correction is interpreted as resulting from the interplay between the information extracted from the system through measurements and the flow of information from the environment to the open system: Due to memory effects single realizations of a dynamical process are no longer independent, and their correlations fundamentally affect the behavior of entropy fluctuations.

PACS numbers: 03.65.Yz, 05.30.Ch, 05.70.Ln

I. INTRODUCTION

Since many years fluctuations in far-from-equilibrium processes have been studied both in a classical [1–3] and in a quantum context [4–6]. The large interest they attract is due, for instance, to their deep connection with equilibrium thermodynamic quantities characterizing a system interacting with an environment [7, 8], as well as with quantum information theory [9]. In the quantum realm the consequences of such an interaction on the fluctuations of physical quantities of the open system has been extensively studied only under the Markovian approximation and/or in the weak coupling limit [10, 11]. Different methods have been developed, allowing for the formulation of some theorems analogous to the well-known classical fluctuation theorems [12–14]. However, an extension of these approaches to non-Markovian processes has only partially been attempted [15] and is far from being a settled problem. Taking into account non-Markovian dynamics in nonequilibrium thermodynamics is, however, an issue of great interest, since recently memory effects have been extensively investigated, both from a theoretical [16–18] and from an experimental point of view [19]. On a more fundamental level, the possibility of characterizing a non-Markovian extension of thermodynamic concepts is very closely related to the investigation on the quantum limits of thermodynamics [20, 21], recently attracting a great deal of attention.

In this work we extend the method developed in Ref. [10] to the non-Markovian regime by employing recently constructed stochastic formulations of classical and quantum non-Markovian master equations [22–24]. In this way we are able to account for memory effects in far-from-equilibrium entropic fluctuations and thus to formulate a non-Markovian generalization of an entropic fluctuation theorem, highlighting also how and why it differs from its Markovian counterpart.

The paper is structured as follows. In Sec. II we define our physical scenario and introduce its general dynamical description. Section III is a brief review of the Markovian

approach of [10], slightly modified to fit with our goals, and explicitly emphasizes the role of the structure of the associated master equation. In this way the reason for which such a method cannot account for non-Markovian processes will become clear. Section IV is devoted to the introduction of the main ideas and results of this work, namely a generalization of [10] which exploits a stochastic unravelling of non-Markovian processes. In Sec. V we comment on the physical interpretation of the non-Markovian fluctuations described by our approach, and present some final remarks and conclusions.

II. THE MASTER EQUATION

We consider an open quantum system with free Hamiltonian H_S , interacting with an environment (free Hamiltonian H_E) via an interaction term H_I . Let us suppose the free Hamiltonian of the open system to show a certain time dependence caused by some parameters being externally modified in time. Such an external modification drives the system far from its initial equilibrium (or stationary) state and towards a final state characterized by different values of these control variables. During its evolution the system interacts with its environment, our goal being to study the effect of such an interaction on fluctuations of thermodynamic quantities. We employ a time-convolutionless (TCL) master equation [25] for the open system density matrix $\rho(t)$, describing a general quantum dynamics:

$$\frac{d}{dt}\rho(t) = \mathcal{K}(t)\rho(t), \quad (1)$$

where

$$\begin{aligned} \mathcal{K}(t)\rho = & -i[H(t), \rho] \\ & + \sum_i \gamma_i(t) \left[A_i(t)\rho A_i^\dagger(t) - \frac{1}{2} \{A_i^\dagger(t)A_i(t), \rho\} \right]. \end{aligned} \quad (2)$$

The Hamiltonian $H(t)$ in Eq. (2) describes the unitary part of the open system evolution, which is given by its

free Hamiltonian $H_S(t)$ plus a renormalization term due to the interaction with the bath. The nonunitary part of the evolution, describing dissipation and dephasing, is accounted for by a set of generally time-dependent Lindblad operators $A_i(t)$ and corresponding relaxation rates $\gamma_i(t)$. Equation (1) describes Markovian as well as non-Markovian processes in terms of a master equation which is local in time [26].

The starting point of our analysis on nonequilibrium entropic fluctuations is the expression for thermodynamic ensemble quantities, and in particular for the time variation of the von Neumann entropy along the nonequilibrium dynamics itself. To this end, we write the state of our open quantum system as [10]

$$\rho(t) = \sum_a \mu_a(t) |a(t)\rangle \langle a(t)|, \quad (3)$$

where the set $\mathfrak{B}(t) = \{|a(t)\rangle\}$ is a time-dependent orthonormal basis of the open system Hilbert space instantaneously diagonalizing $\rho(t)$, and $\sum_a \mu_a(t) = 1$. Using the generator of the dynamics given in (2) and calculating the mean value of Eq. (1) for a state $|b(t)\rangle \in \mathfrak{B}(t)$, one easily obtains a Pauli-type master equation for the evolution of the populations $\mu_a(t)$,

$$\dot{\mu}_b(t) = \sum_a \left(R_{ba}(t) \mu_a(t) - R_{ab}(t) \mu_b(t) \right), \quad (4)$$

where the total instantaneous transition rate $R_{ba}(t)$ between two states $|a(t)\rangle$ and $|b(t)\rangle$ belonging to $\mathfrak{B}(t)$ is defined as

$$R_{ba}(t) = \sum_i \gamma_i(t) |\langle b(t) | A_i(t) | a(t) \rangle|^2. \quad (5)$$

These transition rates will turn out to be crucial in the expression for all thermodynamic quantities of interest. Moreover, it is their time behavior which we employ to characterize the occurrence of memory effects during the process: As will be discussed in more detail in Sec. IV, the process described by the Pauli master equation (4) is defined to be non-Markovian if and only if at least one of the transition rates $R_{ba}(t)$ between two particular instantaneous eigenstates of $\rho(t)$ temporarily becomes negative.

III. THE MARKOVIAN CASE

In the case of a purely (and possibly time-dependent) Markovian dynamics, the rates given by Eq. (5) never become negative. In what follows we will use indices a and b to label vectors in the instantaneous eigenbasis of $\rho(t)$ (recall Eq. (3)), and an index i to label the possible decay channels described by the set of Lindblad operators $A_i(t)$ in (2). We will furthermore, for the sake of brevity, sometimes suppress the time arguments of the instantaneous eigenvectors and eigenvalues of $\rho(t)$.

A. Entropies

Evaluating the von Neumann entropy in the instantaneous eigenbasis of $\rho(t)$, we obtain its time derivative \dot{S} in the form

$$\dot{S}(t) = - \sum_b \dot{\mu}_b(t) \ln \mu_b(t). \quad (6)$$

Using Eq. (4) in Eq. (6) we find

$$\dot{S}(t) = - \sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{\mu_b(t)}{\mu_a(t)}. \quad (7)$$

A similar expression was derived in Ref. [10], but the use of a TCL master equation in our approach allows us to express transition rates explicitly in terms of Lindblad operators. This clarifies the physical framework we are working in and, as will become evident in Sec. IV, explicitly shows where and how memory effects come into play in the case of non-Markovian dynamics.

Having at our disposal the expression for the time derivative of entropy, and following usual prescriptions of nonequilibrium thermodynamics [27, 28], we can write Eq. (7) as a sum of two different contributions as $\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t)$, having defined

$$\dot{S}_e(t) = - \sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{R_{ba}(t)}{R_{ab}(t)}, \quad (8)$$

$$\dot{S}_i(t) = \sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{\mu_a(t) R_{ba}(t)}{\mu_b(t) R_{ab}(t)} \quad (9)$$

as, respectively, the entropy flux between system and environment and the total entropy production. Equations (7), (8) and (9) describe the time dependence of entropy due to the ensemble dynamics described by a TCL master equation. The irreversibility of the process is characterized by a nonzero rate of entropy production $\dot{S}_i(t)$ inside the system which, furthermore, in the case of a Markovian dynamics never becomes negative. It is worth stressing that the definition (9) for the entropy production coincides with the negative time derivative of the relative entropy of $\rho(t)$ and the stationary state ρ_{stat} of the dynamics, provided the latter exists and detailed balance holds.

B. Fluctuations

The above defined quantities characterize the physics of the open quantum system on an ensemble level. Such a picture, while allowing us to derive suitable expressions for many quantities of interest, lacks however a characterization of single nonequilibrium processes and, in particular, of their intrinsically fluctuating physical quantities. The goal of this section is to obtain a fluctuation theorem for the entropy production along single realizations of the ensemble dynamics. By definition, a fluctuation theorem

for a quantity Q characterizing a thermodynamic system is an expression for the ratio of the probability of such a quantity having the value q along a particular nonequilibrium process, and the probability of the same quantity having a value $-q$ along the backward realization of the same process. In order to describe these fluctuations we employ the master equation (4) which in the present case only involves positive transition rates and can thus be regarded as a differential Chapman-Kolmogorov equation for a classical, Markovian stochastic jump process with, in general, time-dependent rates $R_{ba}(t)$. Let us consider a particular, yet generic realization of this process,

$$|a_0(t_0)\rangle \rightarrow |a_1(t_1)\rangle \rightarrow \cdots \rightarrow |a_N(t_N)\rangle, \quad (10)$$

consisting of N jumps at times t_1, t_2, \dots, t_N between well defined states belonging to the instantaneous eigenbases of $\rho(t)$. According to the master equation (4) the probability of the trajectory (10) can be written as

$$p_f = \mu_{a_0}(t_0) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} d\tau \sum_b R_{ba_j}(\tau)} \times \prod_{j=0}^{N-1} R_{a_{j+1}a_j}(t_{j+1}) dt_{j+1}, \quad (11)$$

where the first factor gives the probability for the system to start its trajectory in the state $|a_0\rangle$, the second factor gives the probability that there are no jumps between the times t_j and t_{j+1} , and the third factor represents the probability of having N jumps within infinitesimal time intervals dt_j around t_j between the states of the trajectory (10).

It is important to emphasize that the stochastic description given by Eq. (11) is based on the Pauli-type master equation (4) and thus correspond to the standard stochastic unraveling of a classical Markovian master equation [29], in which the probability for a transition from state $|a(t)\rangle$ to state $|b(t)\rangle$ during the time interval dt is determined by $R_{ba}(t)dt$ with the rate given by Eq. (5). Thus we follow here the interpretation proposed in [10] to identify the fluctuations of single nonequilibrium processes with those described by the evolution equation (4) for the populations of the density matrix. This interpretation and the underlying physical picture has to be carefully distinguished from the interpretation of the stochastic wave function methods (see, e.g., Ref. [30] and references therein) for the open system dynamics given by a quantum master equation of the form of Eq. (1) in terms of a continuous measurement of the environment.

The backward process corresponding to (10) is described by the trajectory

$$|a_N(t_N)\rangle \rightarrow |a_{N-1}(t_{N-1})\rangle \rightarrow \cdots \rightarrow |a_0(t_0)\rangle. \quad (12)$$

The probability p_b for such a backward process is defined analogously to what has been done for the forward one, taking into account the jumps in the sequence given in Eq. (12) such that the conditioned non-jump evolution

probability is then the same for forward and for backward processes, while the jump rates are reversed,

$$p_b = \mu_{a_N}(t_N) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} d\tau \sum_b R_{ba_j}(\tau)} \times \prod_{j=0}^{N-1} R_{a_j a_{j+1}}(t_{j+1}) dt_{j+1}. \quad (13)$$

Thus, we find that the logarithm of the ratio of the two probabilities takes the form

$$\ln \frac{p_f}{p_b} = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)} + \sum_{j=0}^{N-1} \ln \frac{R_{a_{j+1}a_j}(t_{j+1})}{R_{a_j a_{j+1}}(t_{j+1})}. \quad (14)$$

The first term

$$\Delta s = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)} \quad (15)$$

represents the change of the von Neumann entropy, while

$$\Delta s_e = - \sum_{j=0}^{N-1} \ln \frac{R_{a_{j+1}a_j}(t_{j+1})}{R_{a_j a_{j+1}}(t_{j+1})} \quad (16)$$

yields the entropy flux integrated along a single trajectory. The average over all possible trajectories leads to the expressions (7) and (8), respectively. Defining

$$\sigma = \Delta s - \Delta s_e \quad (17)$$

as the total entropy production along a single trajectory, we thus obtain an entropic fluctuation theorem for Markovian dynamics,

$$\frac{p_f(\sigma)}{p_b(-\sigma)} = e^\sigma, \quad (18)$$

from which the quantum analog of Crooks theorem [31] and the quantum Jarzynski equality [32] directly follow.

IV. THE NON-MARKOVIAN CASE

What happens if we introduce memory effects into the dynamics? The generator (2) of the TCL master equation describing a non-Markovian time evolution keeps the same structure as before, but the decay rates $\gamma_i(t)$ can temporarily become negative. This allows us to describe in full generality any non-Markovian quantum process, the TCL formulation being very general, requiring only the map to be invertible and differentiable with respect to time [33]. We are going to study the thermodynamic consequences of this behavior. An attempt to take into account negative decay rates in the formulation of a fluctuation theorem has already been performed in [15] where, however, a clear formulation of a non-Markovian fluctuation theorem was not given. In particular the approach of

[15] works well as long as the transition rates $R_{ba}(t)$ stay positive, which however is the characterization we gave of a Markovian process. A study of nonequilibrium fluctuations, then, has not been performed yet for the class of processes which we define as non-Markovian. What we are going to develop is, on the contrary, a formulation valid in any case, also including our definition of non-Markovianity.

A. Renormalized entropies

Analogously to what has been done in the Markovian case, we start by analyzing the entropic ensemble behavior of the open quantum system. The equation for the time derivative of von Neumann entropy, Eq. (7), is of course the same, but now the time evolution of populations is affected by memory effects. To see where exactly these effects come into play, let us closely analyze Eq. (4) which follows from any TCL master equation, either Markovian or not. Such an expression for $\dot{\mu}_b(t)$ depends on the transition rates $R_{ba}(t)$ defined in (5). Notice however that each term in the sum on the right-hand side of (5) is proportional to a decay rate $\gamma_i(t)$ which, in the non-Markovian case, may cause the whole sum to temporarily become negative. To deal with this, let us rewrite the total transition rates as

$$R_{ba}(t) = R_{ba}^M(t) - R_{ba}^{NM}(t), \quad (19)$$

where the Markovian contribution $R_{ba}^M(t)$ and the non-Markovian contribution $R_{ba}^{NM}(t)$ are defined by

$$R_{ba}^M(t) = \frac{1}{2} [|R_{ba}(t)| + R_{ba}(t)], \quad (20)$$

$$R_{ba}^{NM}(t) = \frac{1}{2} [|R_{ba}(t)| - R_{ba}(t)]. \quad (21)$$

With these definitions, Eq. (7) can be rewritten as

$$\dot{S}(t) = - \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right) \ln \frac{\mu_b(t)}{\mu_a(t)}. \quad (22)$$

The occurrence of memory effects has the consequence of reducing the rate of change of entropy of the system during certain intervals of time. It is possible, as shown, to separate the non-Markovian contribution to the change of von Neumann entropy and to prove that such a contribution always counteracts the Markovian one.

The next step is now to define entropy flux and entropy production for the analyzed process. In particular it is interesting to investigate the possibility of singling out non-Markovian contributions in these two quantities, as done for the von Neumann entropy itself. We then proceed as before, writing

$$\dot{S}(t) = \dot{\mathcal{S}}_e(t) + \dot{\mathcal{S}}_i(t), \quad (23)$$

where formally both $\dot{\mathcal{S}}_e(t)$ and $\dot{\mathcal{S}}_i(t)$ are the entropy flux and production for the ensemble dynamics, and have the

same expression as in the Markovian case, but they are fundamentally different because of the new structure of the transition rates $R_{ba}(t)$. Indeed, we have

$$\begin{aligned} \dot{\mathcal{S}}_e(t) = & - \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right) \\ & \times \ln \frac{R_{ba}^M(t) - R_{ba}^{NM}(t)}{R_{ab}^M(t) - R_{ab}^{NM}(t)}, \end{aligned} \quad (24)$$

$$\begin{aligned} \dot{\mathcal{S}}_i(t) = & \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right) \\ & \times \ln \frac{\mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right)}{\mu_b(t) \left(R_{ab}^M(t) - R_{ab}^{NM}(t) \right)}. \end{aligned} \quad (25)$$

However these quantities, as already highlighted in [15], involve logarithms of not necessarily positive terms and may become temporarily ill-defined (although both the von Neumann entropy and its time derivative are of course always mathematically well-defined). Moreover, it is not possible to clearly isolate a Markovian and a non-Markovian contribution to these quantities, since the arguments of both logarithms involve Markovian and non-Markovian effects in a non-factorizable way.

How is it then possible to speak about ensemble entropy production along non-Markovian dynamics? The appearance of negative rates is, by our definition, the characterization of non-Markovianity and, moreover, it is known that these rates cannot all be negative at the same time, which means there will always be at least one negative ratio involved in the definition of entropy flux and production. To overcome this problem, let us consider again Eq. (23). It simply amounts to writing the time derivative of von Neumann entropy as a sum of two contributions, each of which may involve the logarithm of a negative number. Notice however that, apart from the factor μ_a/μ_b (which can be written as an additional logarithmic term in the sum), the arguments of each logarithm in $\dot{\mathcal{S}}_e(t)$ and $\dot{\mathcal{S}}_i(t)$ are the same. If we replace all negative ratios R_{ba}/R_{ab} under the logarithms by their moduli $|R_{ba}/R_{ab}|$, the decomposition of $\dot{S}(t)$ into the two contributions still holds, since $\ln |R_{ba}/R_{ab}|$ is added and subtracted in the sum. It is thus natural to define entropy flux and production for the non-Markovian ensemble dynamics as

$$\begin{aligned} \dot{\mathcal{S}}_e(t) = & - \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right) \\ & \times \ln \frac{|R_{ba}^M(t) - R_{ba}^{NM}(t)|}{|R_{ab}^M(t) - R_{ab}^{NM}(t)|}, \end{aligned} \quad (26)$$

$$\begin{aligned} \dot{\mathcal{S}}_i(t) = & \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) - R_{ba}^{NM}(t) \right) \\ & \times \ln \frac{\mu_a(t) |R_{ba}^M(t) - R_{ba}^{NM}(t)|}{\mu_b(t) |R_{ab}^M(t) - R_{ab}^{NM}(t)|}. \end{aligned} \quad (27)$$

These definitions coincide with the ones given in Eqs. (24) and (25) when the latter are real quantities, and extend them to general non-Markovian ensemble dynamics. Equations (22) and (27) clearly show how memory effects manifest themselves in backflows of information from the environment to the system as now $\dot{S}_i(t)$ can become negative.

There is however a second problem which is closely connected to the very definition of a fluctuation theorem: As in the Pauli master equation (4) some rates are negative, it is not possible to give it a pure state single trajectory description. Nevertheless, it is possible to proceed along a slightly different path which will indeed lead to a theorem for out-of-equilibrium fluctuations. To this end, consider Eq. (22) which is exact and directly stems from the TCL master equation we started from. It can be rewritten as follows,

$$\begin{aligned}\dot{S}(t) &= - \sum_{a,b} \mu_a(t) \left(R_{ba}^M(t) + \frac{\mu_b(t)}{\mu_a(t)} R_{ab}^{NM}(t) \right) \ln \frac{\mu_b(t)}{\mu_a(t)} \\ &= - \sum_{a,b} \mu_a(t) T_{ba}(t) \ln \frac{\mu_b(t)}{\mu_a(t)}.\end{aligned}\quad (28)$$

where we have introduced positive *renormalized* transition rates

$$T_{ba}(t) = R_{ba}^M(t) + \frac{\mu_b(t)}{\mu_a(t)} R_{ab}^{NM}(t). \quad (29)$$

Since positive transition rates characterize Markovian dynamics we can exploit these renormalized rates to define effective Markovian-like flux and production for the open system entropy by means of

$$\dot{S}_e^r(t) = - \sum_{a,b} \mu_a T_{ba} \ln \frac{T_{ba}}{T_{ab}}, \quad (30)$$

$$\dot{S}_i^r(t) = \sum_{a,b} \mu_a T_{ba} \ln \frac{\mu_a T_{ba}}{\mu_b T_{ab}}. \quad (31)$$

These two quantities are always well defined from a mathematical point of view, and their sum just gives back Eq. (22). The microscopic motivation for these definitions will be given in Sec. IV B. For now let us just look at Eqs. (30) and (31) as effective quantities, which on one hand solve the problem of negative arguments of the logarithms, and on the other hand reduce to Eqs. (8) and (9) in the limit of a Markovian dynamics. We can consider these quantities as the Markovian part of the expressions (26) and (27). The remaining part, which can not be effectively described as Markovian and which is thus irreducibly non-Markovian, is given by the difference between the quantities (26) and (27), obtained as a direct extension of the Markovian ones, and the renormalized quantities (30) and (31),

$$\begin{aligned}\dot{S}_X(t) &\equiv \dot{S}_e(t) - \dot{S}_e^r(t) = \dot{S}_i^r(t) - \dot{S}_i(t) \\ &= \sum_{a,b} \mu_a T_{ba} \ln \frac{T_{ba} |R_{ab}|}{|R_{ba}| T_{ab}}.\end{aligned}\quad (32)$$

We note that the quantity $\dot{S}_X(t)$ is zero if all the renormalized transition rates are equal to the original ones, i.e., if all transition rates $R_{ba}(t)$ are positive and there are no signatures of memory effects.

B. Non-Markovian fluctuations

In order to formulate non-Markovian fluctuations of physical quantities along single trajectories we first observe that the master equation (4) can be rewritten in terms of the renormalized transition rates (29) as

$$\dot{\mu}_b(t) = \sum_a \left(T_{ba}(t) \mu_a(t) - T_{ab}(t) \mu_b(t) \right). \quad (33)$$

This form of the master equation is strongly suggested by Eq. (28) for the time derivative of the von Neumann entropy and the corresponding decomposition into renormalized entropy flux and production given by Eqs. (30) and (31). Note that Eq. (33) holds for both Markovian and non-Markovian processes, and that the renormalized rates $T_{ba}(t)$ are always positive by construction. As discussed in [24], the form (33) of the master equation emerges if one interprets a negative rate R_{ba} for a transition from state a to state b as an effective positive rate for the reversed transition which is given by $T_{ba} = \frac{\mu_b}{\mu_a} |R_{ab}|$ according to Eq. (29). Thus, we suggest employing the master equation (33) for the description of fluctuations along single realizations of nonequilibrium processes. It should be noted however that in the non-Markovian case the transition rates $T_{ba}(t)$ depend on the occupation probabilities and that, therefore, different trajectories are no longer independent which expresses the presence of memory effects [23, 34].

Considering again a particular forward trajectory given by (10) we then find the corresponding probability

$$\begin{aligned}p_f &= \mu_{a_0}(t_0) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} d\tau \sum_b T_{ba_j}(\tau)} \\ &\quad \times \prod_{j=0}^{N-1} T_{a_{j+1}a_j}(t_{j+1}) dt_{j+1},\end{aligned}\quad (34)$$

simply by replacing the original transition rates by the renormalized ones. Correspondingly, the probability for the backward trajectory is given by

$$\begin{aligned}p_b &= \mu_{a_N}(t_N) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} d\tau \sum_b T_{ba_j}(\tau)} \\ &\quad \times \prod_{j=0}^{N-1} T_{a_j a_{j+1}}(t_{j+1}) dt_{j+1},\end{aligned}\quad (35)$$

and we obtain for the logarithm of the ratio of forward and backward probability

$$\ln \frac{p_f}{p_b} = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)} + \sum_{j=0}^{N-1} \ln \frac{T_{a_{j+1}a_j}(t_{j+1})}{T_{a_j a_{j+1}}(t_{j+1})}. \quad (36)$$

The first term on the right-hand side is again equal to the change of the von Neumann entropy Δs along the trajectory (see Eq. (15)). In analogy to the Markovian case, the second term represents the negative of the entropy flux integrated along the trajectory, i. e. we have (compare with Eq. (16))

$$\Delta s_e^r = - \sum_{j=0}^{N-1} \ln \frac{T_{a_{j+1}a_j}(t_{j+1})}{T_{a_j a_{j+1}}(t_{j+1})}. \quad (37)$$

Defining the renormalized single trajectory entropy production

$$\sigma_r = \Delta s - \Delta s_e^r \quad (38)$$

we immediately obtain from Eq. (36):

$$\frac{p_f(\sigma_r)}{p_b(-\sigma_r)} = e^{\sigma_r}. \quad (39)$$

Thus, we have found a fluctuation theorem for non-Markovian processes which is formally identical to the one obtained for Markovian dynamics, see Eq. (18). However, in the non-Markovian case the fluctuation theorem holds for the renormalized entropy production σ_r which can be written as

$$\sigma_r = \Delta s - \Delta s_e + \Delta s_X = \sigma + \Delta s_X, \quad (40)$$

where Δs_X is the single trajectory contribution to the time integral over $\dot{S}_X(t)$ (see Eq. (32)). In the Markovian case Δs_X vanishes and Eq. (39) reduces to Eq. (18). This means that in general only a part of the entropy production, namely the one originating from the fluctuations described by the form (33) of the master equation can be described in terms of a fluctuation theorem. The fluctuation theorem for non-Markovian processes is thus fundamentally different from its Markovian counterpart, as it describes fluctuations of the entropy production of single processes, which are not the single trajectory contribution to the ensemble entropy production (27).

To interpret the result (39) in physical terms we first note that within our approach fluctuations are described by the stochastic unraveling of the master equation (33). However, as has been emphasized already, due to the presence of memory effects single trajectories are not independent of each other or, in other words, they are correlated. Due to these correlations a single realization of a nonequilibrium non-Markovian process thus yields on average more information than just the one described by its associated entropy production. This is why the measured renormalized entropy production, obtained in this work as σ_r in Eq. (40), is given by the usual single trajectory entropy production σ *plus* an additional term which alters the usual Markovian form of the fluctuation theorem. This term, given by Δs_X in Eq. (40), represents the

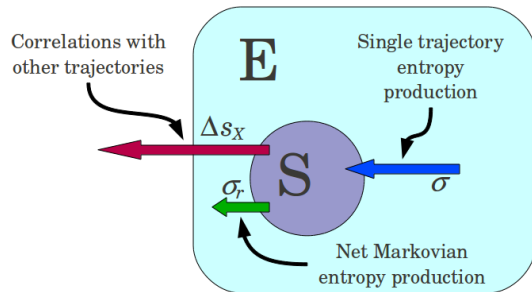


FIG. 1. (Color online) Schematic view of the contributions to the entropy production along single nonequilibrium trajectories according to Eq. (40). The net Markovian information flux σ_r , which obeys the fluctuation theorem (39), is equal to the sum of the single trajectory entropy production σ and the non-Markovian contribution Δs_X due to correlations between trajectories.

additional information extracted from the system originating from the correlations between single trajectories. As we have demonstrated these contributions combine such that their sum obeys the fluctuation theorem (39), completely analogous to the classical and the quantum Markovian one (see Fig. 1).

V. CONCLUSIONS

The analysis of Sec. IV shows that, when taking into account memory effects in a quantum thermodynamics context, there is a close link between fluctuations in entropy production along single realizations of nonequilibrium processes and the existence of an irreducibly non-Markovian entropic contribution in the ensemble dynamics. Any time the dynamics shows signatures of memory effects, a quantum fluctuation theorem has to take into account the full information contribution of the dynamics, which is no longer given only by the ensemble entropy production. More precisely, when a single trajectory is taken into account, memory effects produce an additional term to the information an external observer can reveal by measurements. Such an additional measured information contribution originates from the existence of correlations between single trajectories, which in turn is a consequence of memory effects. This can be clearly seen from Eq. (33), as the differential equations for the time evolution of populations are no longer linear due to the structure of renormalized rates, Eq. (29). Performing a measurement of entropy production along a single trajectory, then, means also extracting information about any other possible trajectory, and we have demonstrated that this extracted information leads to a net entropy production which effectively behaves as a Markovian one. It is this effective Markovian entropy production along single trajectories whose fluctuations can be described by means of a fluctuation theorem of the usual form. The

effective Markovian entropy production is obtained as the sum of the single trajectory contribution to ensemble entropy production and the information on trajectories correlations extracted by measurements. Quite remarkably, these two terms combine together in such a way that their sum behaves according to a very simple fluctuation law.

Thus, due to non-Markovian features the measurement of fluctuating quantities affects the fluctuations themselves. In a sense, the fluctuations we reveal in our approach do not describe only single trajectory properties but supply information on the whole set of possible real-

izations of a thermodynamic process and on their mutual dependence. The renormalization of rates performed in Eqs. (30) and (31) is, indeed, nothing but the mathematical counterpart of the scheme depicted in Fig. 1. We expect, however, that the fluctuation theorem (39) might undergo more deep modifications if one considers other measurement schemes in order to characterize single trajectories, such as stochastic wave function unravellings expressing a continuous monitoring of the environment. This point could be an important and fruitful subject of future works in this field.

-
- [1] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
 - [2] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
 - [3] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005).
 - [4] S. Deffner and E. Lutz, Phys. Rev. Lett. **107**, 140404 (2011).
 - [5] M. Esposito, U. Harbola and S. Mukamel, Rev. Mod. Phys. **81**, 1665 (2009).
 - [6] M. Campisi, P. Hänggi and P. Talkner, Rev. Mod. Phys. **83**, 771 (2011).
 - [7] A. Suárez, R. Silbey and I. Oppenheim, Phys. Rev. E **85**, 051108 (2012).
 - [8] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco Jr. and C. Bustamante, Science **296**, 1832 (2002).
 - [9] D. Kafri and S. Deffner, Phys. Rev. A **86**, 044302 (2012).
 - [10] M. Esposito and S. Mukamel, Phys. Rev. E **73**, 046129 (2006).
 - [11] M. Esposito and C. Van den Broeck, Phys. Rev. Lett. **104**, 090601 (2010).
 - [12] M. Esposito and K. Lindenberg, Phys. Rev. E **77**, 051119 (2008).
 - [13] S. Deffner, M. Brunner and E. Lutz, Europhys. Lett. **94**, 30001 (2011).
 - [14] F. Liu, Phys. Rev. E **86**, 010103(R) (2012).
 - [15] T. Kawamoto and N. Hatano, Phys. Rev. E **84**, 031116 (2011).
 - [16] H.-P. Breuer, E.-M. Laine and J. Piilo, Phys. Rev. Lett. **103**, 210401 (2009).
 - [17] A. Rivas, S. F. Huelga and M. B. Plenio, Phys. Rev. Lett. **105**, 050403 (2010).
 - [18] E.-M. Laine, H.-P. Breuer, J. Piilo, C.-F. Li, G.-C. Guo, Phys. Rev. Lett. **108**, 210402 (2012).
 - [19] B.-H. Liu, L. Li, Y.-F. Huang, C.-F. Li, G.-C. Guo, E.-M. Laine, H.-P. Breuer and J. Piilo, Nature Physics **7**, 931 (2011).
 - [20] J. Gemmer, M. Michel and G. Mahler, *Quantum Thermodynamics*, Lect. Not. Phys. **784** (Springer-Verlag, Berlin, 2010).
 - [21] C. Jarzynski, Annu. Rev. Condens. Matter Phys. **2**, 329 (2011).
 - [22] J. Piilo, S. Maniscalco, K. Härkönen and K.-A. Suominen, Phys. Rev. Lett. **100**, 180402 (2008).
 - [23] J. Piilo, K. Härkönen, S. Maniscalco and K.-A. Suominen, Phys. Rev. A **79**, 062112 (2009).
 - [24] E.-M. Laine, K. Luoma and J. Piilo, J. Phys. B: At. Mol. Opt. Phys. **45**, 154004 (2012).
 - [25] F. Shibata, Y. Takahashi and N. Hashitsume, J. Stat. Phys. **17**, 171 (1977); S. Chaturvedi and F. Shibata, Z. Phys. B **35**, 297 (1979).
 - [26] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University, Berlin, 2002).
 - [27] J. Schnakenberg, Rev. Mod. Phys. **48**, 571 (1976).
 - [28] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
 - [29] D. T. Gillespie, J. Phys. Chem. **81**, 2340 (1977).
 - [30] M. B. Plenio and P. L. Knight, Rev. Mod. Phys. **70**, 101 (1998).
 - [31] M. Esposito, U. Harbola and S. Mukamel, Phys. Rev. E **76**, 031132 (2007).
 - [32] M. Campisi, P. Talkner and P. Hänggi, Phys. Rev. Lett. **102**, 210401 (2009).
 - [33] P. Štelmachovič and V. Bužek, Phys. Rev. A **64**, 062106 (2001).
 - [34] H.-P. Breuer and J. Piilo, EPL **85**, 50004 (2009).